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# Preparation of new proton exchange membranes using sulfonated poly(ether sulfone) modified by octylamine (SPESOS)

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## A B S T R A C T

Sulfonated poly(arylene ether sulfone) (SPES) has received considerable attention in membrane preparation for proton exchange membrane fuel cell (PEMFC). But such membranes are brittle and difficult to handle in operation. We investigated new membranes using SPES grafted with various degrees of octylamine. Five new materials made from sulfonated polyethersulfone sulfonamide (SPESOS) were synthesized with different grades of grafting. They were made from SPES, with initially an ionic exchange capacity (IEC) of 2.4 meq g<sup>-1</sup> (1.3 H<sup>+</sup> per monomer unit). Pristine SPES with that IEC is water swelling and becomes soluble at 80 °C, its proton conductivity is in the range of 0.1 S cm<sup>-1</sup> at room temperature in aqueous H<sub>2</sub>SO<sub>4</sub> 1 M, similar to that of Nafion<sup>®</sup>. After grafting with various amounts of octylamine, the material is water insoluble; membranes are less brittle and show sufficient ionic conductivity. Proton transport numbers were measured close to 1.

### Keywords:

Polymers

Electrochemical properties

Glass transitions

Nuclear magnetic resonance (NMR)

## 1. Introduction

Proton exchange membranes (PEM) are key components in many electrochemical processes: electro dialysis, water treatment, energy storage in electrolyzers and Redox systems and fuel cells (PEMFC) which have been recognized as promising new energy conversion technologies for clean power sources. Commercially available perfluorinated PEM, such as Nafion<sup>®</sup>, are commonly used due to their excellent chemical and oxidative resistance as well as high proton conductivity, in the range of 0.1 S cm<sup>-1</sup>. However, their drawbacks are high cost and low operation temperature and have motivated researches on alternative proton conducting membranes to the perfluorinated membranes for high temperature PEMFC applications [1]. Many promising polymers are based on polyaromatic thermoplastics [1–4], such as poly(aryl ether ketone) (PAEK/PEEK), poly(ether sulfone) (PES), and polybenzimidazole (PBI) which have high chemical and thermal stability, low cost and an easier processing. The functionalization by sulfonation of these polymers leads to improved membrane properties (better wettability, higher water flux, better perm selectivity) and makes these sulfonated polymers good candidates for PEM materials. Examples include sulfonated polyether–ether ketones [5–7], sulfonated polyimides [8–10], sulfonated polybenzimidazole [11,12],

sulfonated polystyrene [13,14] and sulfonated polyether sulfone [15–19].

Polyethersulfone thermoplastics, widely used as membranes in dialysers, in ultra filtration and for reverse osmosis, exhibit a high resistance to hydrolysis. This resistance, combined with easiness for chemical modification and processing via casting, were decisive in selecting this polymer. In this paper, our choice was based on poly(bisphenol A sulfone) commercially available as UDEL P-3500<sup>®</sup> from Solvay, which can be easily sulfonated as described in [19].

The proton conducting properties of PEMs for sulfonated aromatic polymers rely on proton solvation by water at high water activities: massive water uptake leads thus to a high proton conductivity of the hydrated membranes. The critical point of such membranes remains however the mechanical properties: dry membranes are brittle and hydrated membranes may exhibit a dramatic loss of mechanical properties.

As a strategy to improve proton conductivity and mechanical properties of the membranes, many approaches have been proposed. A first approach consists in incorporating in the membrane small inorganic particles, such as silica or zirconium phosphates [20]. A more classical approach is to develop sulfonated block copolymers, with the incorporation of soft units in stiff polymer backbones, which could provide the membrane with better flexibility. Many sulfonated block copolymers have been reported, such as sulfonated-fluorinated poly(arylene ether)s [21], sulfonated polysulfone-block-PVDF copolymers [22], poly(ether ether ketone)-block-sulfonated polybutadiene [23]. More recently, graft-

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## Nomenclature

S-PESOS	sulfonated polyethersulfone octylsulfonamide
S-PES	sulfonated polyethersulfone
PEMFC	proton exchange membrane fuel cell
IEC	ionic exchange capacity
PEM	proton exchange membrane
PES	polyethersulfone
PBI	polybenzimidazole
PEEK	polyetheretherketone
NMR	nuclear magnetic resonance
TGA	thermo gravimetric analysis
DSC	differential scanning calorimetry
DMA	dynamical and thermomechanical analysis
MEA	membrane electrode assembly
TMSCIS	trimethylsilane chlorosulfonate
$W_{dry}$	dry weight
$W_{Wet}$	hydrated weight
$\tau$	water uptake
$\sigma$	ionic conductivity
$R_{membrane}$	resistance of the membrane
$S$	surface
$l$	thickness of the membrane
$t_{H^+}$	proton transport number

ing the sulfonic acid groups to specific chain segments in the polymer was shown to result in the formation of well-defined hydrophilic/hydrophobic phase-separated structures (like in the Nafion<sup>®</sup> membrane), inducing effective proton conduction [24,25]. Still, nowadays, none of these membranes could compete with Nafion membranes.

In this paper, a new simple strategy is proposed. It consists in keeping the polyaromatic skeleton of PES, and grafting pending chains of octylamine, which results in an increased flexibility. Our paper describes the results obtained by grafting octylamine groups at various proportions. The material has been characterized by <sup>1</sup>H RMN, TGA and DSC. Membranes have been cast and characterized by DMA, conductimetry, transport numbers and water swelling.

## 2. Experimental part

### 2.1. Materials used

Poly(ether sulfone) (UDEL P-3500<sup>®</sup>) was received from Solvay Polymer. That polymer has average molecular weights in the range between 20,000 and 50,000 g mol<sup>-1</sup> and  $T_g$  close to 185 °C. It is soluble in various organic solvents such as methylene chloride, tetrahydrofuran, dimethylformamide and dimethylacetamide. It is stable up to 400 °C in air.

Chlorotrimethyl silane, chlorosulfonic acid were received from Aldrich. Petroleum ether, dichloromethane, tetrahydrofuran and methanol were received from VWR, hydrochloric acid was received from LauryLab, phosphorous pentachloride was received from Fluka, octylamine and dimethylacetamide were received from Acros. All chemicals were used without further purification.

### 2.2. Apparatus

The NMR spectra were recorded an AC200 Bruker spectrometer (200 MHz) at room temperature. The polymer sample (40 mg mL<sup>-1</sup>) were dissolved in DMSO-d6 ( $\delta = 2.49$  ppm for <sup>1</sup>H NMR).

Differential scanning calorimetry (DSC) measurements are done using TA Instrument. A sample (3 mg) of polymer is put in the cell and the thermogram is registered between 20 and 225 °C with a sweep rate of 5 °C min<sup>-1</sup> under an argon flow of 40 mL min<sup>-1</sup>.

The thermo gravimetric analysis (TGA) was carried out using a Perkin Elmer TGA 6. The approximately 5 and 10 mg samples were first dried at 100 °C to remove any moisture and solvent for 8 h, and then programmed from 30 to 400 °C at a rate of 7 °C min<sup>-1</sup> under a 40 mL min<sup>-1</sup> nitrogen flow.

Electrical resistances were measured with a Hameg Instrument Conductimeter, LC-meter HM 8018, 160 Hz. The conductivities of proton exchange membranes were measured using a conductimetric clamp in 1 M H<sub>2</sub>SO<sub>4</sub>, as described in [26].

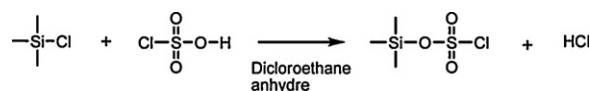


Fig. 1. Synthesis of trimethylsilyl chlorosulfonate (TMSCIS).

Hittorf cell: the cell is symmetrical, constituted by two glass compartments, each of 50 mL, the membrane being clamped between them. The electrodes were made on platinized expanded titanium. The electrode surface is 4.15 cm<sup>2</sup>. The cell was filled with aqueous H<sub>2</sub>SO<sub>4</sub> 1 M. Current densities were chosen as 100, 75 and 40 mA during respectively 188, 243 and 430 mn. The amount of proton transfer is close to 11 mmol, the initial proton content in every compartment being 100 mmol. Fig. 8 gives the principle of the method [26,27].

Dynamic mechanical analysis (DMA) measurements were carried out with a TA Instruments DMA Q800 spectrometer working in the tensile mode. Membrane samples were cut with the following dimensions: length 11 mm, width 5 mm, thickness 0.2 mm. Measurements were performed in isochronal conditions (1 Hz) and the temperature was varied between 0 °C and 300 °C at 3 °C min<sup>-1</sup> under a flow of dry air of 50 mL min<sup>-1</sup>.

A membrane electrode assembly (MEA) was created using PaxiTech<sup>®</sup> electrodes (F-38130 Echirolles). The 64 cm<sup>2</sup>-membrane was sandwiched between an hydrogen electrode and an oxygen electrode, these two electrodes having a Pt-quantity of 0.5 mg Pt cm<sup>-2</sup>. The fuel cell performances were recorded at ambient temperature and under atmospheric pressure ( $P(\text{H}_2)$  and  $P(\text{O}_2)$  equal to 1 atm).

## 3. Polymer modification

Sulfonation of poly(ether sulfone) was carried out in dichloromethane by stepwise addition of trimethylsilane chlorosulfonate (TMSCIS) (Fig. 1). The process, similar to that described in [3], was carried under argon atmosphere and anhydrous conditions, gaseous HCl being evacuated promptly, in order to avoid any polymer chain breakage. TMSCIS is a relatively mild but efficient reactant allowing a sulfonation of 1.3  $-\text{SO}_3\text{H}$  group per monomer unit. The mixture is stirred at 40 °C during 24 h under argon bubbling. The resulting solution is then poured progressively into an ethanol solution of sodium ethanolate. The sodium salt of SPES  $\text{SPES}(\text{Na}^+)$  precipitates. After filtration, the product is washed by ethanol, then by petroleum ether. It is dried during 72 h (yield = 95%).

The acidic form of SPES  $\text{SPES}(\text{H}^+)$  was obtained by ion exchange from SPES ( $\text{Na}^+$ ) with Amberlite IR-120, acid form at room temperature. Water is then evaporated and the product dried at 70 °C under vacuum (yield = 88%).

The chlorosulfonated form of S-PES ( $-\text{SO}_2\text{Cl}$  groups) was obtained from the sodium salt by reaction with phosphorous pentachloride under argon atmosphere. In a three necked flask, 50 g (0.17 mol of monomer unit) of S-PES ( $\text{Na}^+$ ) are put in anhydrous dichloroethane (2 L). 10 mL of dimethylformamide are added to initiate the reaction. Phosphorous pentachloride ( $\text{PCl}_5$ ) (0.36 mol) 72.09 g is added portion wise (exothermic). Stirring of the orange solution is maintained during 12 h, resulting NaCl is filtered off, and the limp solution is poured in 6 L of methanol. The polymer precipitates, is filtered, washed with methanol and dried at 100 °C under vacuum. The product is kept under argon atmosphere (yield = about 100%).

Grafting of octylamine: five kinds of polymer grafted with octylamine have been prepared with various rates of grafting. Five identical solutions are prepared with 6 g (0.0104 mol of monomer unit) of SPES (Cl) dissolved in 100 mL of tetrahydrofuran and kept under argon atmosphere at 60 °C. The following quantities of octylamine are added in every solution: first solution 0.52 mL (0.00314 mol), second solution: 0.692 mL (0.00418 mol), third solution: 0.87 mL (0.00526 mol), fourth solution: 1.03 mL (0.00628 mol), fifth solution: 6.95 mL (0.0421 mol) (Table 1). The solutions are kept under stirring during 6 h at 60 °C. After cooling at room temperature, any solid is filtered off, and the solution poured in 500 mL of petroleum ether. The polymer is filtered out and washed with HCl (1 M) aqueous solution for hydrolysis of resid-

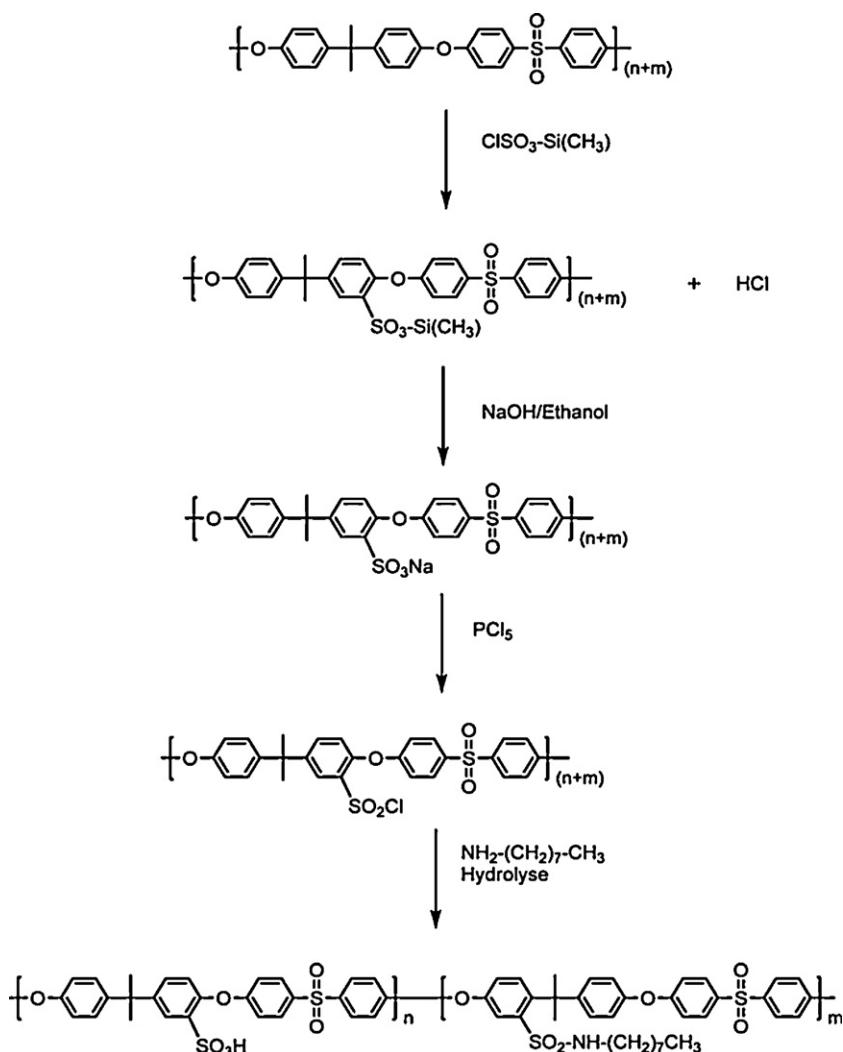


Fig. 2. Synthesis reaction of S-PESOS.

ual  $\text{SO}_2\text{Cl}$  and elimination of unreacted amine. The polymer is then washed with water until the rinsing water keeps neutral. It is finally dried at  $80^\circ\text{C}$  for 12 h (Fig. 2). Yields are given in Table 1.

The degree of sulfonation and the amount of octylamine grafted are confirmed by NMR (Figs. 3 and 4). Samples are dissolved in DMSO- $d_6$ . The peak at 1.65 ppm is assigned to SPES methyl group, the peak at 0.8 ppm to the octylamine methyl group. Ethanol (precipitating solvent) impurity may be detected at 1.2 and 3.7 ppm (triplet and quadruplet). Signal at 1.2 ppm is assigned to octylamine methylene groups ( $-\text{CH}_2$ ) $_7$ , and signal at 2.6 ppm is assigned to the octylamine methylene group vicinal to ( $-\text{NH}-$ ). Integration of the different signals allows the determination of the grafted octylamine and sulfonic acid group amounts (Table 2). The amount of sulfonic

acid is given by the ratio of signal A to signal B areas corresponding to aromatic protons (Fig. 3), using the following relation. The calculation is made on ungrafted SPES. This formula has been described and demonstrated in [19].

$$R = \frac{\int B}{\int A} = \frac{17.474}{10} = 1.7474$$

$$f = \frac{12 - 4R}{2 + R} = 1.3 \text{ H}^+ \text{ mol}^{-1}$$

$$F = \frac{1000 \cdot f}{M + m \cdot f} = 2.38 \text{ H}^+ \text{ kg}^{-1}$$

The results, given in Table 1, show that the non-grafted membranes give the maximal ion exchange capacity ( $2.38 \text{ meq g}^{-1}$ ) and that the increase of grafted octylamine leads to a decrease of the degree of sulfonation.

## 4. Preparation and characterization of membranes

### 4.1. Preparation of membranes

Pristine or grafted SPES is dissolved in dimethylacetamide (DMA) at room temperature in order to have a solution 10% by

**Table 1**  
Various degree of sulfonation of different membranes synthesized.

	Quantities of octylamine (equivalent of mol)	Ion exchange capacity IEC ( $\text{meq g}^{-1}$ )	Yield (%)
S-PES	0	2.38	98
S-PESOS	1.3	0	82
S-PESOS	0.3	1.91	85
S-PESOS	0.4	1.75	77
S-PESOS	0.5	1.58	98
S-PESOS	0.6	1.40	96
Nafion <sup>®</sup> 117	-	1.2	-

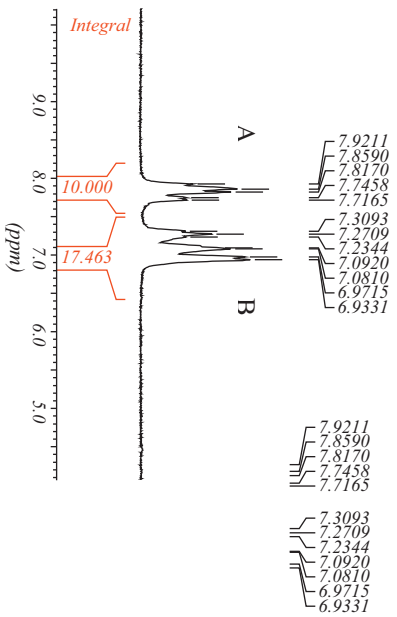


Fig. 3. <sup>1</sup>H NMR spectra of S-PES (2.38 meq g<sup>-1</sup>).

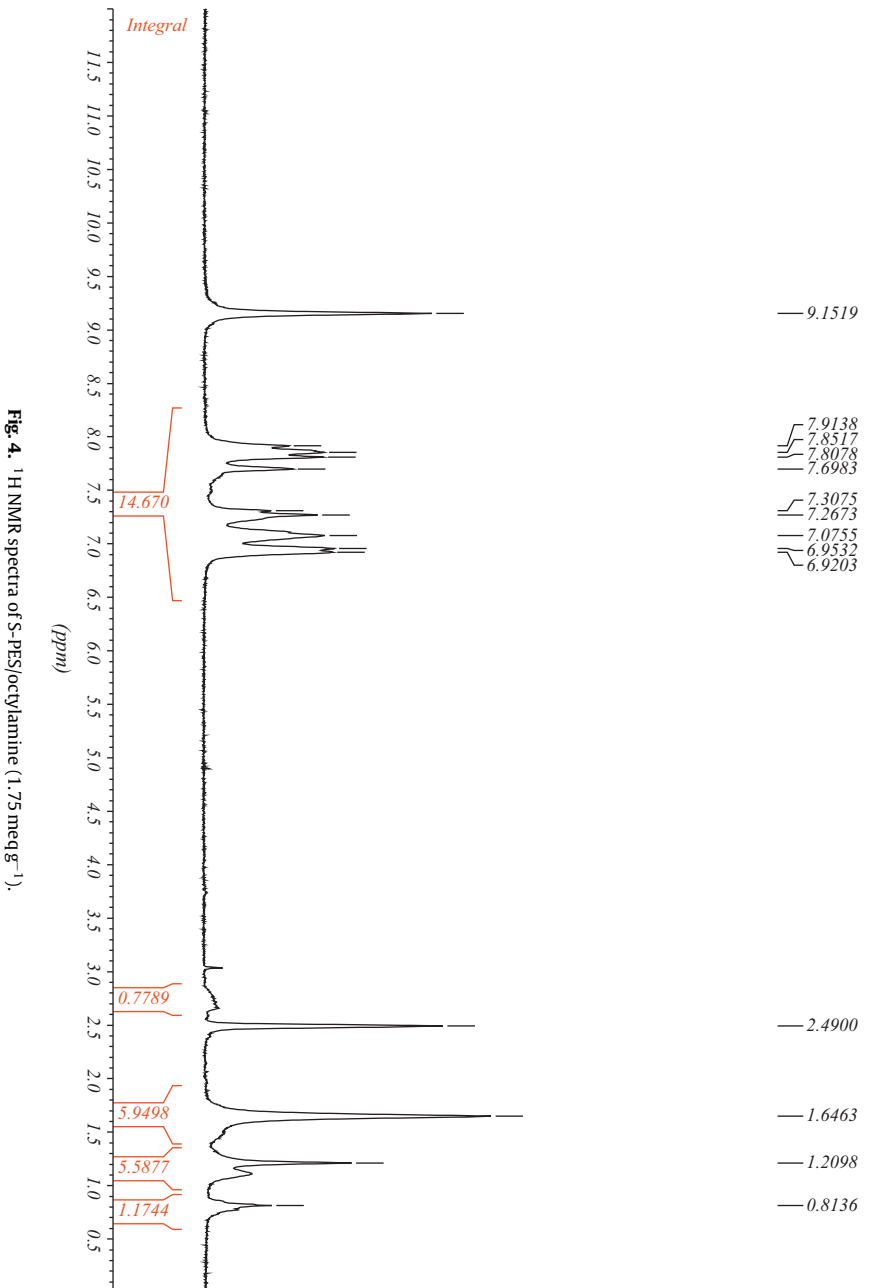
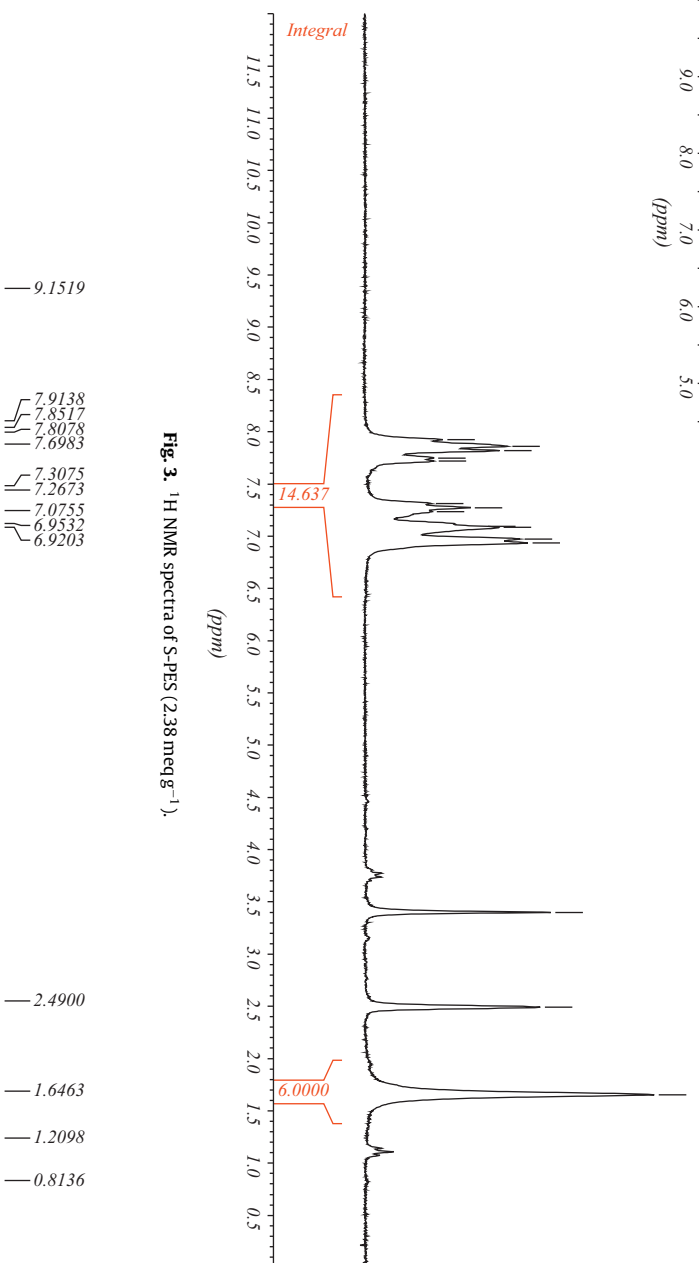


Fig. 4. <sup>1</sup>H NMR spectra of S-PES/octylamine (1.75 meq g<sup>-1</sup>).



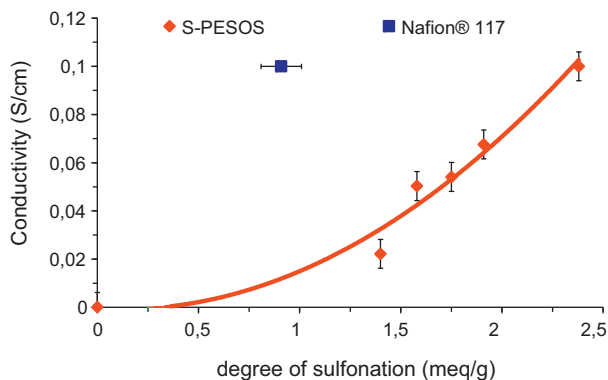


Fig. 6. Ionic conductivity of various synthesized membranes.

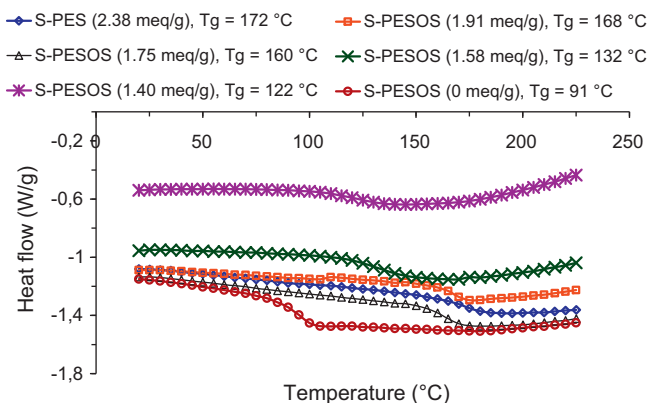


Fig. 7. DSC curves of polymers synthesized.

#### 4.4. Proton transport number (Hittorf's cell)

When the transport number of proton equals to one, the amount of protons in every compartment should not change, proton production at the anode compensates the proton transfer through the membrane, itself compensating the proton reduction to dihydrogen at the cathode. The proton concentration may vary slightly in each compartment, because some water is electrolysed, proton is migrating with solvating water, and some water evaporation may occur. Accurate measurements are difficult and fair reliability is obtained by assessment of the proton content

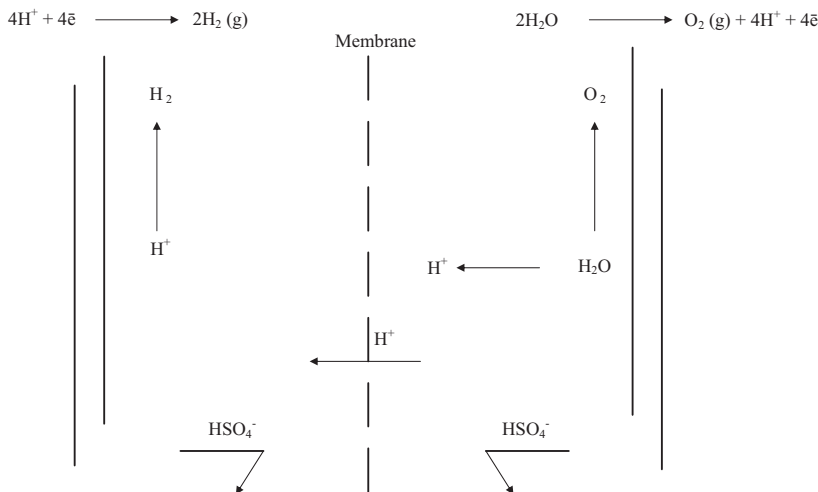


Fig. 8. Principle of transport numbers.

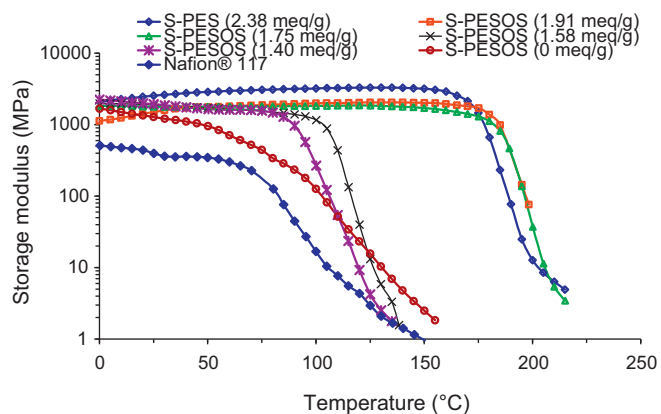


Fig. 9. DMA study of various synthesized membranes.

in both compartments,  $Q_0$  at the beginning,  $Q_f$  at the end of the electrolysis. Proton selectivity may also depend on the current density, but our method cannot ascertain if some water dissociation into proton and hydroxyl anion occurs at the anodic surface of the membrane. Determination of  $Q_0^a$ ,  $Q_0^c$  and  $Q_f^a$ ,  $Q_f^c$  in the anodic (respectively cathodic) compartment determines the anodic (respectively cathodic) initial and final transport number computed from the following formula:

$$t_a^{(H^+)} = \frac{(Q_0^a - Q_f^a) F}{It} + 1 \quad t_c^{(H^+)} = \frac{(Q_f^c - Q_0^c) F}{It} + 1$$

Results are given in Table 3. Within experimental errors, the membranes are selectively proton conducting whatever the amount of octylamine grafting.

#### 4.5. Dynamical and thermomechanical analysis (DMA)

The different membranes display similar typical behaviour: in the glassy state ( $T < 100$  °C), the tensile storage modulus  $E'$  remains roughly constant and very high, which explains the high embrittlement of the membranes. Then around a temperature comprised between 100 °C and 200 °C, we observe a modulus drop, associated with the glass transition. It appears that the glass transition temperature, at which occurs this drop, depends on the rate of octylamine grafting. Results are shown in Fig. 9.



**Table 3**  
Transport numbers of all synthesized membranes.

	Surface (cm <sup>2</sup> )	Time (mn)	Current intensity (mA)	$t^+$ cathodic	$t^+$ anodic
S-PES (2.38 meq g <sup>-1</sup> )	4.15	188	100	0.99	0.98
S-PES (2.38 meq g <sup>-1</sup> )	4.15	243	70	0.99	0.99
S-PES (2.38 meq g <sup>-1</sup> )	4.15	430	40	0.99	0.98
S-PESOS (1.91 meq g <sup>-1</sup> )	4.15	188	100	0.98	0.98
S-PESOS (1.91 meq g <sup>-1</sup> )	4.15	243	70	0.99	0.99
S-PESOS (1.91 meq g <sup>-1</sup> )	4.15	430	40	0.99	0.99
S-PESOS (1.75 meq g <sup>-1</sup> )	4.15	188	100	0.98	0.97
S-PESOS (1.75 meq g <sup>-1</sup> )	4.15	243	70	0.96	0.92
S-PESOS (1.75 meq g <sup>-1</sup> )	4.15	430	40	0.99	0.99
S-PESOS (1.58 meq g <sup>-1</sup> )	4.15	188	100	0.99	0.97
S-PESOS (1.58 meq g <sup>-1</sup> )	4.15	243	70	0.99	0.97
S-PESOS (1.58 meq g <sup>-1</sup> )	4.15	430	40	0.99	0.99
S-PESOS (1.40 meq g <sup>-1</sup> )	4.15	188	100	0.99	0.98
S-PESOS (1.40 meq g <sup>-1</sup> )	4.15	243	70	0.99	0.99
S-PESOS (1.40 meq g <sup>-1</sup> )	4.15	430	40	0.99	0.98
Nafion® 117	4.15	188	100	0.99	1.00
Nafion® 117	4.15	243	70	1.00	1.00
Nafion® 117	4.15	430	40	0.99	0.99

The effect of the octylamine grafting is in accordance with that observed in DSC: it tends to lower the glass transition temperature and thus to reduce the brittleness of the membrane. For the SPES octylamine (0.8 H<sup>+</sup> mol<sup>-1</sup>) and (0.7 H<sup>+</sup> mol<sup>-1</sup>) membranes, the glass transition temperature is comprised between 120 and 135 °C, which is quite similar to Nafion Tg (Fig 7).

#### 4.6. Membrane-electrode assembly

Assemblies were carried out with the different membranes and the fuel cell performances, recorded at ambient temperature and under atmospheric pressure, are shown Fig. 11 and are compared to the Nafion 117. It is noteworthy that no measurement was possible with the non-grafted membrane (2.38 meq g<sup>-1</sup>), since the membrane was too brittle and broke in the MEA.

## 5. Discussion

Literature describing the use of sulfonated polyaromatics is rather scarce, although a large number of papers describes the formation and properties of pure or modified membranes such as sulfonated polyether ketones or polyether sulfones. Among polyether sulfones prepared from bisphenol A, UDEL P-3500® is especially interesting because the monomer unit presents two benzene rings where sulfonation can occur. Sulfonation is easily performed up to 1.3 sulfonic group per monomer unit. Such an amount of sulfonic groups is usually unnecessary for most applications, especially fuel cells, because the polymer becomes

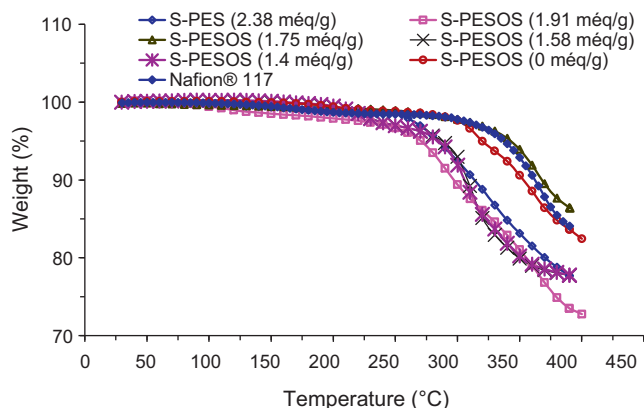
water-soluble at high temperature (>80 °C) when the sulfonic contents increase above 0.8 groups per monomer unit. But above this amount, excess sulfonic groups may be used for modifying the polymer, enhancing its softness and lowering its solubility. We designed a process for obtaining a polymeric backbone with 1.3 (-SO<sub>2</sub>Cl) group per monomer unit, without any reticulation by (-SO<sub>2</sub>-) groups bridging the chains. This is a very important result, since (-SO<sub>2</sub>Cl) groups are very reactive and can be used at will for grafting different kinds of substrates on the chain.

We present here the results obtained with octylamine. That substrate is common, easy to handle, the -NH<sub>2</sub> group is reactive, the aliphatic chain is flexible (polyethylene has a Tg below -30 °C). The resulting sulfonamide group is resistant to hydrolysis and oxidation.

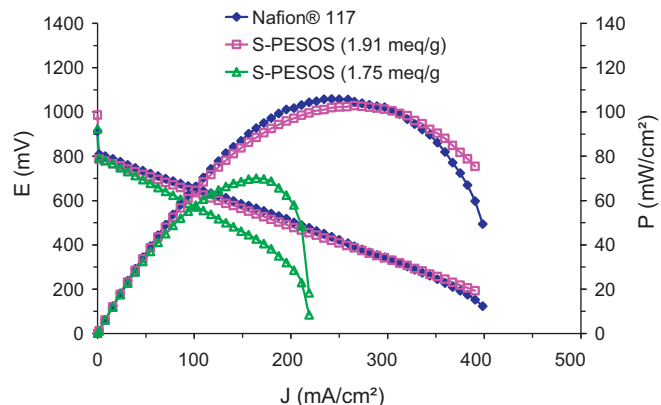
The grafting of octylamine is quantitative, and the rate of grafting can be chosen at will, as demonstrated by NMR analysis (Table 3). The resulting material is thermally stable as demonstrated by DSC and TGA experiments (Figs. 7 and 10).

Pristine SPES (2.4 meq g<sup>-1</sup>, 1.3 H<sup>+</sup> mol<sup>-1</sup>) shows a glass transition temperature (Tg) of 172 °C. Glass transition temperatures of octylamine grafted SPES are shifted to lower temperatures, up to 92 °C for the fully grafted SPES. The results of glass transition temperature collected by DSC are in agreement with those obtained by DMA.

The glass transition temperatures are lowered if sufficient amount of octylamine is grafted. The resulting material is insoluble in water and in aliphatic hydrocarbons, but can be dissolved



**Fig. 10.** Thermal stability of all polymers synthesis.



**Fig. 11.** Fuel cell performances, Paxitech® S = 64 cm<sup>2</sup>, H<sub>2</sub> and O<sub>2</sub> flow rates = 324 and 517 mL min<sup>-1</sup>, respectively.



in solvents such as DMSO, dimethylacetamide or other polar aprotic solvents. Membranes can be cast from these solutions. They appear to be homogeneous, transparent, much less brittle than the ungrafted membranes and flexible when wet. They are easy to handle. Thermomechanical dynamic analysis on dry membranes confirms the properties observed by DSC (Fig. 7).

All acidic polymers synthesized show two weight loss stages. The first weight loss at around 100 °C is related to the adsorption of water bonded to the sulfonic groups. The second weight loss is assigned to the decomposition of sulfonic groups. A comparison between the TGA of SPES (2.4 meq g<sup>-1</sup>) and all SPESOS synthesized show no differences in the range of fuel cell application. The decomposition of sulfonic groups of acidic SPES (2.4 meq g<sup>-1</sup>) started at 250 °C and the decomposition of sulfonamide groups of SPESOS (0 meq g<sup>-1</sup>) started at 300 °C. Hence, the sulfonic groups decomposed faster than the sulfonamide groups.

In the SPESOS membranes (1.91, 1.75 and 1.40 meq g<sup>-1</sup>) the two steps of decomposition (sulfonic and sulfonamide) could be noticed. Results are shown in Fig. 10.

Dynamical and thermomechanical behaviour of the samples of membranes have been compared. Their storage moduli behave similarly upon variation of temperature. They are rigid at low temperature and flexible near the glass transition temperature. Thermomechanical properties are dependant upon the rate of octylamine grafting, as shown in Fig. 9. Softening occurs when the rate of grafting is higher than 0.4 octylamine per monomer unit.

Water swelling is not excessive (<50% per weight) when the grafting is sufficient ( $\geq 0.3$  octylamine per monomer unit). Unless the membrane is totally grafted, the conductivity is sufficient for most possible applications: fuel cells, electrolysers, electro dialysis, etc.

This is confirmed by the first preliminary results obtained in fuel cells (Fig. 11). Membranes having similar conductivities to the Nafion 117 membrane (Fig. 6) exhibit similar performances in fuel cells. For example, the power density of these cells with SPESOS membranes (1.91 meq g<sup>-1</sup>) reaches nearly 110 mW cm<sup>-2</sup> at room temperature, which is similar to the fuel cells containing Nafion 117. It is quite encouraging to reach the same performances as the Nafion 117 but with a much less expensive membrane. Further measurements at 80 °C are in progress.

The values of conductivity are high and do not represent the intrinsic conductivity of membranes SPESOS without sulfuric acid. Normally, the results of conductivity should be obtained by impedancemetry at relative humidity and temperatures controlled [28]. But our figures give a good idea of the trend of conductivity as a function of grafting grade, as compared to Nafion 117 in the same conditions (Fig. 6). It is clear that softness is obtained at the detriment of conductivity. Experiments are under progress for improving the conductivity of SPESOS membranes without loosing the softness.

Furthermore the different membranes were proved to be ion selective with proton transfer numbers close to one. This result will be extended to other ions. Much more work has still to be done for obtaining the scope and limitations of that kind of materials, but our preliminary experiments demonstrate that sulfonated polyaromatics afford very interesting materials with certainly a large scope of possible modifications.

## 6. Conclusion

Sulfonated poly(ether sulfone), with different rate of sulfonation has been prepared as described in [19]. But the SPES with 1.3 SO<sub>3</sub>H per monomer unit (2.4 meq g<sup>-1</sup>) is a completely new synthesis. A

process has been designed for the quantitative transformation of -SO<sub>3</sub>H groups into SO<sub>2</sub>Cl groups, without any reticulation by -SO<sub>2</sub>- bridges. From that material, octylamine has been grafted on the PESS backbone at various degrees of grafting. <sup>1</sup>H NMR confirms the quantitative grafting of octylamine. After hydrolysis the material contains sulfonamide and sulfonic acid groups in predetermined proportions. DSC measurement shows a lowering of the glass transition temperature when the amount of octylsulfonamide is higher than 0.3 groups per monomer unit. The resulting material has been cast in membranes. The membranes show a smooth variation of ionic conductivity and water uptake in relation with the amount of grafted octylamine. In H<sub>2</sub>SO<sub>4</sub> solutions the selectivity of the membrane is very high for proton transport. DMA determinations show that the softness of the membranes has been increased by octylamine grafting. The TGA curves show a good stability of SPESOS in the temperature range for fuel cell application. Such membranes may be used for the usual applications of proton conducting polymer membranes, for example fuel cells. Grafting of other substrates than octylamine is currently under progress.

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